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An Introduction to Polymeric Electrolyte Alkaline Anion Exchange Membranes

Jince Thomas[1], Minu Elizabeth Thomas[2], Bejoy Francis[3], and Sabu Thomas[1]

[1] Mahatma Gandhi University, International and Inter University Center for Nanoscience and Nanotechnology, Kottayam 686560, Kerala, India
[2] Mahatma Gandhi University, School of Polymer Science and Technology, Kottayam 686560, Kerala, India
[3] Mahatma Gandhi University, St. Berchmans College, Department of Chemistry, Kottayam 686101, Kerala, India

1.1 Introduction

Currently, the magnitude of energy usage cannot be denied. It is indispensable in every aspect of life, and a booming population results in increasing energy demand. Recognizing that nonrenewable sources will eventually run out, the value of renewable sources cannot be underestimated because they are sourced from unlimited sources. The most crucial consideration of renewable sources is their environmental impact while using them. The proper use of energy appears to be a major topic these days, and one must decide which type of energy should be used, and why it is vital?

The urgent necessity of researching, developing, and commercializing renewable energy sources and the technologies accompanying them is universally acknowledged as a prime focus. Time and place are essential components of most renewable energy systems. Therefore, it is crucial to build relevant energy conversion and storage devices to capture these unreliable energy sources effectively. The most prominent electrochemical energy storage and energy conversion devices are batteries, electrochemical super capacitors, and fuel cells.

Electrolytes are vital components of electrochemical energy storage and conversion devices, and their properties and performance can significantly impact the overall efficacy, safety, and longevity of these systems. Although electrolytes have been recognized and researched for centuries, their physiological role was not fully understood until the late nineteenth and early twentieth centuries [1, 2]. Starting from that point, researchers delved deeper into the behavior of electrolytes, focusing

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on their conductive properties. This led to the creation of innovative electrochemical techniques and tools, like the pH meter and the potentiometer. Later on, advancements in materials science and engineering resulted in the development of solid-state electrolytes with high ion conductivity, which are widely used in batteries, fuel cells, and electrochromic devices. Nowadays, there is a growing interest in crafting new electrolytes for emerging electrochemical applications, such as energy storage and conversion, electrochemical water treatment, sensing, and biosensing.

1.2 Different Types of Electrolytes

Understanding the classification of electrolytes can provide valuable information about their behavior and properties in different applications, depending on the specific context and purpose. There are various ways to classify electrolytes, such as the type of ions they contain, their physical form, and their conductivity [3]. Below are some of the most frequently used methods for categorizing electrolytes,

- Based on the origin
- The type of ions present
- Its physical state
- Conductivity measure
- The contrast between acidic and alkaline properties

The most popular is the classification based on the physical nature of electrolytes (Figure 1.1). During the early 1970s, researchers began exploring the potential of solid-state materials such as ceramic, glass, crystalline, and polymer electrolytes. This led to various types of polymer electrolytes with different compositions and structures, including solid-state polymer electrolytes (polymer–salt complex), gel

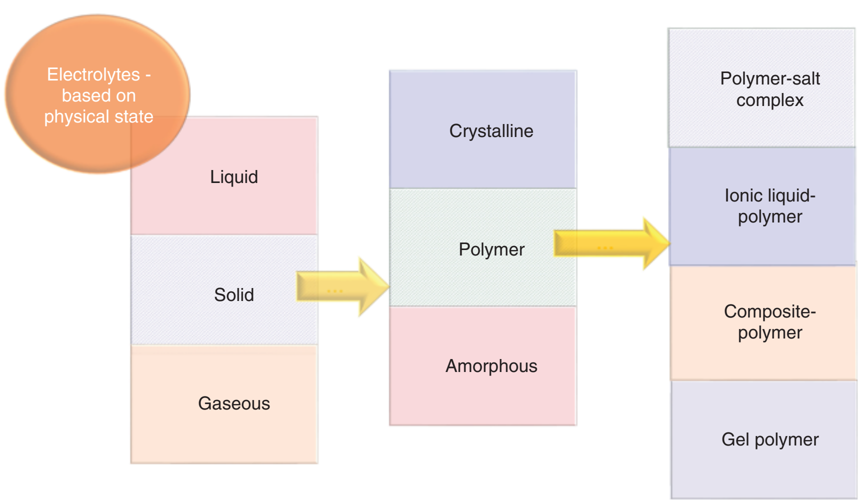

Figure 1.1 Classification of electrolytes.

Table 1.1 Advantages and disadvantages of liquid-state and solid-state electrolytes.

Electrolyte	Advantages	Disadvantages
Liquid	Effortless processing	Gas solubility is low
	Low cost	Change on concentration
	Ionic conductivity is high	Potential window is short
	Using different ions	Parallel reactions
		Interactions with other gases
Solid	A wider potential window	Complex processing
	No parallel reactions	Low ionic conductivity
	Gas solubilization is not required	Expensive
	Low external interferences	

polymer electrolytes, composite polymer electrolytes, and ionic liquid polymer electrolytes.

The solid-state electrolytes have more advantages than conventional liquid electrolytes. The advantages and disadvantages of solid-state and conventional liquid-state electrolytes are presented in Table 1.1.

Our focus is on solid-state electrolytes, specifically polymer electrolytes. A polymer electrolyte is a membrane that has alkali–metal–ion conductivity. It is composed of a polymer matrix as a solvent and solutions of salts that are dissociated within the polymer matrix. Polymer electrolyte is a remarkable solid-state system that showcases impressive ionic conduction abilities, making it an ideal choice for a wide range of electrochemical devices like rechargeable batteries [4], solid-state batteries [5], fuel cells [6], supercapacitors [7], electrochemical sensors [8], electrochromic windows, and analog memory devices [3, 9, 10].

1.3 Why Polymer Electrolytes Are Important?

Polymer electrolytes have distinct advantages over conventional electrolytes, making them essential in many fields and applications. They offer increased safety, especially in high-energy applications like lithium-ion batteries, as they are solid or gel-like, reducing the risk of fire or explosion. Polymer electrolytes also exhibit improved chemical and electrochemical stability, which minimizes electrode degradation and corrosion, leading to better device performance and longer lifespan. They have a broad electrochemical stability window, which enables operation at higher voltages without decomposition, which is critical for high-voltage batteries and supercapacitors. Although their ionic conductivity is lower than that of liquid electrolytes, advancements in polymer chemistry have improved conductivity, expanding their suitability for diverse applications.

Another benefit of polymer electrolytes is their ability to be processed into various shapes and forms, such as thin films or membranes, making them versatile for different device configurations and facilitating complex system integration and device miniaturization. Additionally, many polymer electrolytes are eco-friendly and are made from sustainable and recyclable materials, providing a greener alternative to liquid electrolytes containing hazardous components. Their compatibility with different materials and ability to function in various conditions make them ideal for numerous technologies. Some important benefits to using polymer electrolytes in comparison to traditional liquid electrolytes are

- High ionic conductivity
- Solvent-free
- Reduced leakage
- Safety
- Easy processability
- Thin-film forming ability and transparency
- Light-weight and flexibility

Polymer electrolyte membranes are mainly categorized into two types: anion exchange membranes (AEMs) and cation exchange membranes (CEMs). They are designed in a way that enables them to selectively transport either anions or cations, depending on their characteristics. The two membranes have significant functions in different electrochemical devices. The choice of the membrane is determined by the system's unique needs and ion transport goals. In Table 1.2, a comparison between AEM and CEM is presented.

The choice between AEMs and CEMs is often driven by the electrochemical device's specific requirements and operating conditions. Although AEMs have advantages, like lower cost, the ability to utilize various renewable fuels directly, and higher pH operation, CEMs are also beneficial due to their higher proton conductivity and compatibility with acidic environments. Choosing between AEMs and CEMs depends on

Table 1.2 Comparison of anion exchange membranes and cation exchange membranes.

Properties	AEM	CEM
Ion transport selectivity	Selective transport of anions	Selective transport of cations
pH operating range	Suitable for alkaline environments	Suitable for acidic environments
Requirement of the catalyst	Non-precious metal catalysts	Precious metal catalysts
Hydration tolerance	Excessive hydration can lead to swelling and instability, while insufficient hydration can hinder ion transport	More tolerant to varying water content compared to AEMs
Fuel flexibility	High	Limited

factors like the required pH range, cost, fuel accessibility, and performance objectives. These two types of membranes are essential in the progress of sustainable energy technologies, and their unique features aid in the overall enhancement and refinement of electrochemical devices. To reap the full benefits of ion exchange membranes in electrochemical applications, it is imperative to have a comprehensive comprehension of the pros and cons of AEMs versus CEMs. Thoughtful contemplation is critical.

1.4 Anion Exchange Membrane (AEM)

AEMs are made up of ion-conducting polymers that possess functional groups that attract and transport anions. Their primary purpose is to facilitate the movement of anions, such as hydroxide (OH^-) and bicarbonate (HCO_3^-), while hindering the transfer of cations. The selectively permeable AEMs contain positively charged functional groups that facilitate anion transport while preventing cation crossover. Various materials are utilized in the production of AEMs, including quaternary ammonium ions [11], imidazolium ions [12, 13], guanidinium ions [14–16], phosphonium ions [17], spirocyclic cations [18], carbocations [19], ionic liquids [20], multi-cations [21, 22], and metal cations [23], which are all functionalized with polymers [24].These remarkable functional groups exhibit the fundamental capability of ion exchange by attracting and transporting anions across the membrane while simultaneously maintaining the balance of the overall charge.

1.4.1 Fundamental Concepts of Anion Exchange Membranes as Polymer Electrolytes

Understanding the fundamental concepts underlying AEMs is crucial in grasping their significance in polymer electrolyte applications. These specialized membranes possess unique characteristics that enable them to function effectively and are critical in ensuring effective ion conduction. By recognizing their value, we can unlock the full potential of polymer electrolyte systems. It is crucial to carefully evaluate the membrane's performance under operational conditions, durability, and cost targets to ensure the successful commercial development of the AEM as an electrolyte. These key factors significantly influence the desired properties and demand careful consideration. The membrane is designed to facilitate the transport of anions while blocking the flow of cations, gases, and electrons. Choosing the cationic group is essential to achieve a high concentration of charges in the membrane and ensure sufficient ionic mobility. It is even more critical to select the right cationic group as it directly impacts the chemical stability of the membrane in optimal operating conditions. Also, a viable approach is to augment the ionic groups within the membrane to improve ionic conductivity.

However, the high concentration of the cationic group can adversely affect the mechanical properties due to excessive water absorption. Therefore, it becomes imperative to implement stringent control measures over the membrane's morphology to enhance its mechanical attributes. However, when the membrane is too hydrated or brittle due to intensive dryness, it will deteriorate the membrane's mechanical properties and have a profoundly negative impact on cell performance. Therefore, maintaining the appropriate level of water uptake is crucial for optimal membrane performance.

Thus, in a nutshell, for optimal performance of the AEM, the following requirements are the desired prerequisites:

- High anion conductivity is essential for efficient ion transportation in materials.
- Maintain chemical stability to withstand the effects of the electrolyte environment and avoid degradation.
- Strong and stable materials are essential for device longevity and proper functioning, maintaining structural integrity and minimizing deterioration.
- Need high selectivity for anions to avoid cation crossing.
- Function as an absolute barrier to prevent the passage of undesirable particles like electrons and gases.
- A balance of water uptake and retention is necessary.
- Manufacturable using scalable and cost-effective techniques to ensure their commercial viability.

Thus, to fully maximize the effectiveness of polymer electrolytes in various electrochemical applications, it is crucial to have a solid grasp on the core concepts of AEMs. This includes understanding their selective ion transport, ion exchange capacity, and water uptake. Through the use of precise and meticulous characterization techniques, the researchers were able to confirm these essential parameters.

Several techniques and measurements are employed to evaluate the structural, morphological, chemical, and electrochemical properties of AEMs. These characterizations offer valuable insights into the behavior and performance of AEMs, facilitating their optimization and comprehension. To identify the AEM's chemical structure, the polymer backbone and functional groups are analyzed through spectroscopic techniques like Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR). Furthermore, membrane morphology can be analyzed using microscopic techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM). To evaluate a membrane's chemical stability over time, subjecting them to harsh chemical environments for desired time is necessary. Meanwhile, their mechanical strength can be analyzed by measuring parameters like tensile strength, Young's modulus, and elongation at break. To measure the thickness of AEMs, techniques such as micrometers or profilometers can be used. The swelling behavior of the membrane is related to its dimensional changes upon water absorption, which can also be examined by measuring its thickness.

The ion exchange capacity is an important factor that measures the amount of ion exchange locations in the AEM material. It is calculated using titration methods, wherein the membrane is subjected to a known concentration of an ion, and the number of exchanged ions is measured. The determination of membrane conductivity can be achieved through either electrochemical impedance spectroscopy (EIS) or conductivity measurements conducted under controlled conditions. Water uptake can be evaluated by comparing the weight or volume of the dry membrane to that of the fully hydrated membrane.

Currently, computational simulations and machine learning methods are utilized to explore the properties and efficiencies of AEM. These techniques aid in proposing novel membrane structures, transport mechanisms, and stability, as well as identifying discrepancies and factors that may be challenging to determine through experimental results.

1.4.2 Classification of AEM

Researchers are currently experimenting with new techniques to create membranes that meet the basic requirements necessary for their function. As a result, there are now numerous types of membrane structures, each classified according to their unique morphology [24, 25]. They are

- Heterogeneous
  - Ion solvating polymers
  - Hybrid membranes
- Interpenetrated polymer networks
- Homogeneous
  - Copolymerization of monomers
  - Radiation grafting
  - Chemical modification

A heterogeneous membrane consists of an anion-exchange material embedded within an inert compound. These membranes can be categorized into two types based on their composition. The first type comprises ion-solvating polymers composed of a water-soluble polymeric matrix containing electronegative heteroatoms, hydroxide ions, and plasticizers. This combination results in a material that possesses the polymeric matrix's mechanical properties and the hydroxide ions' electrochemical properties. Materials fabricating ion-solvating polymers include polyethylene oxide (PEO), polyvinyl alcohol (PVA), and chitosan. These polymers exhibit good mechanical properties, and their ionic conductivity at contact electrodes tends to be low due to their thickness and high electrical resistance. On the other hand, hybrid membranes are composed of both organic and inorganic segments. The organic components contribute to the electrochemical properties, while the inorganic elements, typically silica or siloxane, enhance the mechanical properties. Examples of hybrid membranes include combinations of PEO, PVA, and polyphenylene oxide (PPO) with silica (SiO_2) or titanium dioxide (TiO_2). Despite the good mechanical properties of incorporating inorganic components, membranes in this category still suffer from the nonuniformity issue observed in ion-solvating polymers. Consequently, their ionic conductivity remains similar or even lower.

Interpenetrated polymer network membranes, which belong to another class of AEMs, demonstrate higher ionic conductivities compared to heterogeneous membranes. These membranes are created by blending two polymeric materials through cross-linking without promoting the formation of covalent bonds between them.

One of the polymers is hydrophobic and possesses excellent chemical, mechanical, and thermal properties, while the other polymer acts as an ionic conductor. Fabrication of interpenetrated polymer network membranes is simple, and various polymers may be employed, making them cost-effective. The primary focus of research on membranes in this category includes materials such as polyethylene, PVA, polysulfone, and PPO. These membranes exhibit low electrical resistance, high mechanical strength, chemical stability, and durability. However, due to the absence of covalent bonds between the constituent materials, the conductive polymer slowly diffuses out of the membrane over time. This leads to gradual decreases in conductivity and ion exchange capacity. Homogeneous membranes represent another class of AEMs. These membranes are formed using polymers composed of a single material modified to possess ion exchange capacity. The modification involves covalently attaching cationic functional groups to the polymer backbone, creating ionic sites within the membrane along with associated mobile counterions. The classification of homogeneous membranes is based on the specific methods used for functionalization, including copolymerization, radiation grafting, and chemical modification. Detailed discussions on these classifications will be presented in the forthcoming chapters dedicated to this subject.

1.4.3 Pros and Cons of AEM

Understanding the advantages and disadvantages of AEMs is crucial for enhancing their utilization in various electrochemical applications and advancing the development of efficient and long-lasting energy conversion devices. Table 1.3 highlights the pros and cons of using AEMs as an electrolyte.

Table 1.3 Pros and cons of anion exchange membranes.

Pros	Cons
• High ionic conductivity	• Excessive water uptake can lead to swelling and reduced mechanical stability
• Precise control over selective ion transport	• Limited stability at high temperatures
• Operate over a broad pH range	• The diffusion of mobile counterions out of the membrane decreased conductivity and ion exchange capacity over time
• Good resistance to chemical degradation	• Require periodic cleaning or replacement due to the susceptibility to fouling by organic and inorganic species
• Long-term stability in aggressive environments	• Manufacturing complexity and limited material options compared to other membranes
• Exhibit high mechanical strength and resilience	
• Compatible with aqueous electrolytes	
• Manufactured at a reasonable cost	

Researchers and engineers can make educated judgments about selecting, optimizing, and building AEMs for specific applications by knowing their strengths and limits. Addressing the issues with these membranes will result in improved performance, longer lifespan, and wider use of AEM-based systems in the field of energy conversion and storage.

1.4.4 Application of AEM

AEMs are highly adaptable membranes with the unique ability to hinder cations while permitting a selective flow of anions. Their versatility makes them indispensable in numerous industries, ranging from energy to water treatment and beyond. Their ability to control the movement of ions makes them a crucial tool for many vital processes, including separation, purification, and desalination, in addition to their role as electrolytes. The following are some of the significant applications of AEMs.

1. **Electrochemical Energy Conversion:** Alkaline fuel cells (AFCs) and alkaline water electrolyzers frequently use AEMs, which are electrochemical devices. In AFCs, AEMs facilitate the electrochemical reaction by transporting hydroxide ions (OH^-) from the cathode to the anode. In alkaline water electrolyzers, AEMs play a crucial role in separating gases by selectively conducting hydroxide ions.
2. **Water Treatment:** AEMs are useful in different water treatment methods like electrodialysis and electro-deionization. They serve to eliminate undesired anions, specifically nitrates, sulfates, and chlorides, from water sources, which is beneficial for both water purification and desalination.
3. **Electrodialysis:** AEMs have the vital function of letting only anions pass through the membrane while preventing the migration of cations in electrodialysis. This crucial process facilitates separating and eliminating undesired ions from a solution.
4. **Electrochemical Sensors:** AEMs can be integrated with ion-selective electrodes to identify specific anions present in solutions. These AEM-based sensors are extensively used for environmental monitoring, water quality analysis, and industrial process control.
5. **Chlor-alkali Industry:** The chlor-alkali industry is responsible for producing chlorine gas (Cl_2), sodium hydroxide (NaOH), and hydrogen gas (H_2) via the electrolysis of saltwater. AEMs are utilized as ion exchange membranes in the electrolytic cells to facilitate this process. These membranes permit the migration of chloride ions (Cl^-) and hydroxide ions (OH^-) while preventing the passage of sodium ions (Na^+), which guarantees the desired separation of products.

The most significant application of AEMs is prominently displayed in the diagrammatical representation of Figure 1.2. AEMs find extensive usage in fuel cell applications, specifically in AFCs. The primary area of research for AEMs is centered on fuel cells, aiming to improve their performance, stability, selectivity, and cost-effectiveness.

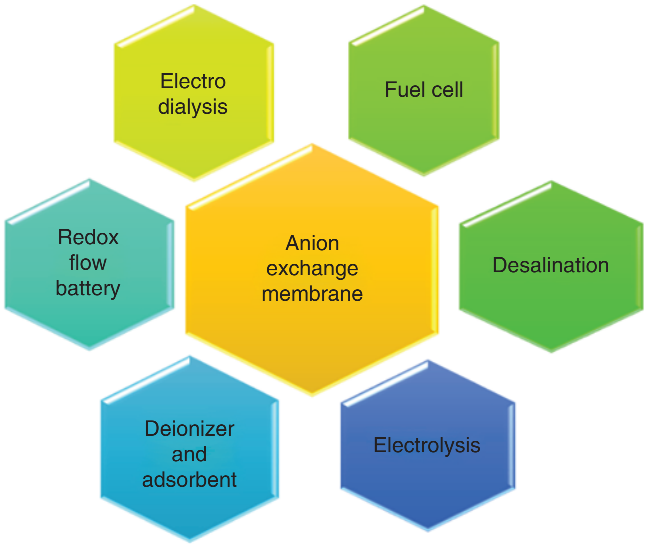

Figure 1.2 Important application of anion exchange membranes.

1.5 AEMs in Fuel Cells

A fuel cell is an energy conversion device that directly converts the fuel's chemical energy into electrical energy by chemically reacting a fuel with an oxidant, usually oxygen from the air. Although the origins of the fuel cell invention are uncertain, two notable individuals are associated with its discovery. Christian Friedrich Schönbein's work on the concept was published in the January 1839 issue of Philosophical Magazine, according to the United States Department of Energy. Meanwhile, Sir William Grove developed the fuel cell and published his findings in the February 1839 issue of the same magazine, as noted by Grimes. Fuel cell technology has grown substantially since its discovery in the nineteenth century. Through the years, researchers and engineers have made significant strides in enhancing fuel cells' efficiency, durability, and practicality. This progress results in the emergence of diverse fuel cell types, each with its distinct features and uses.

The fundamental design of a fuel cell involves an electrolyte layer that separates two electrodes – the anode and the cathode. The electrolyte facilitates the movement of ions while simultaneously preventing any mixing of the fuel and oxidant gases. In the early stages, AFCs utilize a liquid electrolyte solution containing potassium hydroxide (KOH), as it is the most conductive among alkaline hydroxides. Compared to other fuel cells, these AFCs have certain benefits. They are easier to manage as they operate at a relatively lower temperature, have electrodes made of inexpensive metals, and exhibit higher reaction kinetics at the electrodes compared to acidic conditions. However, the sensitivity of the KOH solution to CO_2 limits the AFC's use of liquid electrolytes. Optimal operation requires low CO_2 concentrations in the oxidant stream. If oxygen is replaced with air, the hydroxyl ions may react with CO_2 present in the air, leading to the formation of K_2CO_3. This leads to the precipitation of K_2CO_3 crystals and reduces the availability of hydroxyl ions, leading to decreased efficiency. Incorporating solid electrolytes in proton fuel cells (PFCs) has paved the way for anion-conducting polymer electrolyte membranes to be integrated into AFCs. This move effectively resolves most issues caused by liquid electrolytes, giving rise to a new subfield of AFCs – the anion exchange membrane fuel cell (AEMFC) – and leading to unprecedented growth in the industry. Using a membrane instead of a liquid electrolyte has several advantages. One significant benefit is eliminating the adverse effects of CO_2, which reduces electrode weeping and corrosion. Other membrane benefits include leak-proof properties, volumetric stability, solvent-free conditions, and easy handling. Additionally, the size and weight of the fuel cell are reduced, which expands its potential uses. Thus, AEM is used in an AFC to enhance efficiency and lifespan by slowing down performance degradation over time. It is essential to continue researching and developing AEMs to advance fuel cell technology and facilitate its widespread use as a reliable and eco-friendly energy conversion solution. Although AEM fuel cells have potential advantages and commercial significance, they are still in their early stages of commercialization and have not yet been widely deployed compared to other fuel cell types, such as proton exchange membrane fuel cells (PEMFCs). Nevertheless, there has been growing interest and research in AEM fuel cells.

The demand for clean and sustainable energy solutions is rising, and AEMFCs are gaining commercial significance due to their advantages over other types of fuel cells. AEMFCs use a polymer membrane that is more resistant to degradation, reducing maintenance and replacement costs. They also use low-cost materials, such as non-precious metal catalysts, making them more cost-effective than other fuel cell types. AEMFCs offer fuel flexibility, allowing for the use of various fuels, making them adaptable to different energy sources, and enabling the utilization of existing infrastructure and fuel distribution networks. They have shown promising efficiency levels, potentially converting more fuel energy into usable electrical energy, leading to improved overall energy conversion. Additionally, the polymer membrane used in AEMFCs allows for efficient control of water transport, preventing flooding and facilitating better performance under varying operating conditions. They produce clean electricity without the combustion of hydrocarbon fuels, resulting in lower greenhouse gas emissions and improved air quality.

1.6 Conclusion and Outlook

AEMs as the polymer electrolyte have garnered much attention in electrochemical devices such as fuel cells, batteries, and electrolyzers. AEMs possess unique properties that make them well-suited for various energy conversion and storage applications. Their primary function is to conduct negatively charged ions or anions while impeding the transport of positively charged ions or cations. This selective ion transport is achieved through positive charges or functional groups embedded in the polymer matrix of the membrane. These polymers have excellent mechanical strength, chemical stability, and suitable conductivity for hydroxide (OH^-). The OH^- conductivity is a crucial characteristic of AEMs, enabling efficient anion transport in alkaline environments. Due to their cost-effectiveness, durability, and fuel flexibility, they are highly valued and widely used in commercial settings.

AEM has a broad range of applications. For instance, AEM-based AFCs have shown improved tolerance to carbon monoxide poisoning, enhanced catalyst kinetics, and reduced reliance on expensive platinum catalysts. Compared to other fuel cell types, AEMFCs have these benefits, making them a commercially significant option for clean energy generation in various industries. Additionally, AEMs are widely used in alkaline water electrolyzers, which split water into hydrogen and oxygen using electricity.

One of the significant advantages of AEMs as polymer electrolytes is their ability to operate at low temperatures. Unlike proton exchange membranes (PEMs), which require high operating temperatures, AEMs can function effectively at room temperature or even lower. This feature offers opportunities for developing energy conversion devices that are more cost-effective, efficient, and durable. Moreover, AEMs have environmental benefits, making them a desirable and viable option for the future.

Despite holding great promise in various electrochemical applications, AEMs face challenges such as alkaline stability, ion transport, water management, mechanical stability, and catalyst compatibility. These challenges need to be addressed for widespread adoption. However, with continued research and development, AEM-based devices have the potential to contribute significantly to a cleaner and more sustainable energy future.

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